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The Exchange of Trimethylphosphate on Magnesium(II). A Phosphorus-31 Nuclear Magnetic Resonance Study

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The exchange of trimethylphosphate (TMP) on $Mg(TMP)_6^{2+}$ has been reinvestigated in d_2-methylenechloride and d_6-acetone diluents using ^{31}P NMR spectroscopic methods. The rate of exchange = $6k_{ex}[Mg(TMP)_6^{2+}]$, and a typical set of kinetic data is: k_{ex} (225 K) = 683 ± 47 s^{-1}, $\Delta H^{\#} = 51.3 \pm 0.5$ kJ mol^{-1} and $\Delta S^{\#} = 39.5 \pm 2.0$ J K^{-1} mol^{-1} for a solution in which $[Mg(TMP)_6^{2+}]$, [TMP] and [d_2-methylenechloride] = 0.116, 0.604, and 12.7 mol dm^{-3} respectively. The small variation in k_{ex} (225 K) observed as [TMP] is varied, in conjunction with other evidence, suggests that a D exchange mechanism probably operates. The species $Mg(TMP)_5^{2+}$ is observed in d_2-methylenechloride, and acetone is found to compete with TMP for sites in the first co-ordination sphere of magnesium(II).

Introduction

A knowledge of the mechanism of solvent exchange is fundamental to an understanding of ligand substitution processes on metal ions [1, 2]. As a consequence, the literature on solvent exchange studies is extensive [3, 4] but the bulk of the data therein consists of kinetic parameters determined for the metal ion as solute in the pure solvent. Therefore, mechanistic deductions have largely been made from the observed $\Delta H^{\#}$ and $\Delta S^{\#}$ values which recent analyses have indicated may lead to considerable ambiguity particularly if the sign of $\Delta S^{\#}$ is used to assign molecularity [5–7]. In principle, variation of the co-ordinating solvent concentration by the addition of a non-co-ordinating diluent should permit the determination of the complete solvent exchange rate law and thereby provide a strong indication of the exchange mechanism [7]. In this study we have applied this method to a reinvestigation of the exchange of trimethylphosphate (TMP) on magnesium(II) [8]. This system was selected for study as, firstly, there appears to be no report of a determination of the rate law for solvent exchange on magnesium(II) and, secondly, because the large ^{31}P chemical shifts observed between free and co-ordinated TMP (in contrast to the small chemical shifts observed in the methanol [9], ethanol [10] and TMP [8] (^1H) and water [11] (^{17}O) systems) permits the determination of the exchange process over a large temperature range, and also the observation of different magnesium(II) species.

Experimental

Preparation of the Magnesium(II) Complex

Hydrated magnesium perchlorate (G. Frederick Smith) (2.47 g) was stirred with triethyl orthoformate (14 g) [12, 13] at 330 K for one hour. Atmospheric moisture was excluded during the dehydration reaction by the use of a silica gel guard tube. The solution was transferred to a dry box and trimethylphosphate (6.6 g) slowly added. Crystals of the magnesium complex were then obtained when most of the ethanol was removed under vacuum. Approximately 20 cm^3 of sodium dried ether was added and the mixture allowed to stand for about 30 minutes. The colourless crystals were filtered and washed with anhydrous ether several times before being pumped on a vacuum line for two hours. The yield was 7.5 g. *Anal.* Calcd. for $[Mg(TMP)_6](ClO_4)_2$: Mg, 2.29; C, 20.33; P, 17.47. Found: Mg, 2.37; C, 20.08; P, 17.30. The magnesium(II) analysis was carried out through an ion exchange method [14] six times and the percentage Mg found was 2.37 ± .02 where the error quoted is the standard deviation. It is thus concluded that the stoichiometry is in fact $Mg(TMP)_{5.75}(ClO_4)_2$ for which Mg, 2.37; C, 20.14; P, 17.31. The C and P analyses were carried out by the Australian Microanalytical Service, Melbourne.

Preparation of Solutions

TMP (BDH), d_2-methylenechloride (CEA, France, 99.4%) and d_6-acetone (CEA, France, 99.8%) were carefully distilled and dried over Linde 4A molecular sieves. Solutions in CD_2Cl_2 and $(CD_3)_2CO$ were prepared by weight in 2 cm^3 volumetric flasks under a dry nitrogen atmosphere. Approximately 0.4 cm^3

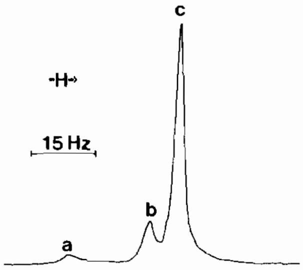

Figure 1. Proton decoupled ^{31}P FT NMR spectrum of a 0.034 mol dm^{-3} solution of $Mg(TMP)_{5.75}(ClO_4)_2$ in d_2-methylenechloride at 167 K. Singlets a) and b) are assigned to $Mg(TMP)_5^{2+}$ and singlet c) to $Mg(TMP)_6^{2+}$.

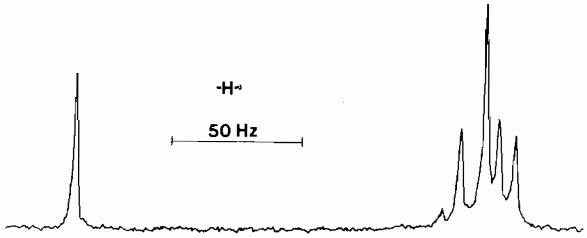

Figure 2. Proton decoupled ^{31}P FT NMR spectrum of a 0.028 mol dm^{-3} solution of $Mg(TMP)_{5.75}(ClO_4)_2$ in d_6-acetone at 176 K. The downfield singlet arises from free TMP.

of each solution was transferred to a 5-mm o.d. NMR tube and degassed prior to sealing under vacuum.

Spectroscopic Measurements

Proton decoupled ^{31}P Fourier Transform NMR spectra were run at 36.43 MHz on a Bruker HX90E spectrometer using a deuterium lock and an 8K data base. The time between pulses was 2.7 s and the tip angle was 40°. At each temperature 500 scans were stored as a 1K data block on a magnetic disk prior to complete line shape analysis. Proton NMR spectra were run in pulsed free precession mode. The spectrometer temperature control was better than ±0.3 °K.

Infrared spectra were run in nujol between NaCl discs on a Perkin Elmer 457 spectrophotometer.

Results and Discussion

The infrared spectrum of $Mg(TMP)_{5.75}(ClO_4)_2$ in nujol shows neither a hydroxyl stretching band nor bands which could be attributed to co-ordinated perchlorate. Therefore the non-stoichiometric formula arising from the elemental analysis suggests the co-existence of both $Mg(TMP)_5^{2+}$ and $Mg(TMP)_6^{2+}$ ions in the solid state. As a crystal structure [15] of the species $[Mg(OAs(Me)_3)_5](ClO_4)_2$ in which the $OAs(Me)_3$ ligands are in square based pyramidal array about magnesium(II) has been reported, and the species $[Mg(OP(Me)_3)_5](ClO_4)_2$ has also been prepared [16], the postulation of the $Mg(TMP)_5^{2+}$ species is in accord with known structures. A TMP complex with the required 2.29% Mg (required for $[Mg(TMP)_6](ClO_4)_2$) has not been prepared in this laboratory and it appears that the earlier reported preparation (Mg = 2.33%) may have been non-stoichiometric also instead of the assumed $[Mg(TMP)_6](ClO_4)_2$ stoichiometry [8].

The proton decoupled ^{31}P NMR spectrum of a 0.034 mol dm^{-3} solution of $Mg(TMP)_{5.75}(ClO_4)_2$ in d_2-methylenechloride at 167 K exhibits three singlets a), b), and c) (Figure 1). The singlets a) and b) are assigned to $Mg(TMP)_5^{2+}$, but spectral resolution did not permit a distinction to be drawn between the square based pyramidal and trigonal bipyramidal geometries which represent the most probable structures for this species. (There may be a minor resonance occurring between a) and b) but it proved impossible to improve resolution beyond that shown in Figure 1.) Singlet c) is assigned to $Mg(TMP)_6^{2+}$, and within the spectral resolution the ratio of the concentration of this species to that of $Mg(TMP)_5^{2+}$ is ~ 3:1. With increase in temperature singlets a), b) and c) coalesce until at 185 K a singlet is observed consistent with rapid interconversion of the five and six co-ordinate species. Addition of TMP ligand (at 175 K) causes singlets a) and b) to simultaneously decrease in intensity and a new singlet assigned to free TMP to appear down field consistent with a shift in equilibrium towards $Mg(TMP)_6^{2+}$. Of solutions i)–v) only solution i) exhibited a small signal (which was <1% of the total coordinated TMP signal) attributable to $Mg(TMP)_5^{2+}$. Within the experimental error the number of TMP molecules in the first co-ordination sphere of magnesium(II) is six in solutions i)–v).

The proton decoupled ^{31}P NMR spectrum of a 0.028 mol dm^{-3} solution of $Mg(TMP)_{5.75}(ClO_4)_2$ in d_6-acetone consists of five resolved coordinated TMP singlets and one free TMP singlet indicating the presence of several species in solution (Figure 2). The appearance of free TMP demonstrates the ability of acetone to displace co-ordinated TMP, and it is probable that as acetone is in excess concentration a co-ordination number of six is retained ($Mg(acetone)_6^{2+}$ has been reported [17] under such conditions) in species of stoichiometry $Mg(TMP)_{6-n}(acetone)_n^{2+}$ in this system. Direct confirmation of the presence of co-ordinated acetone was obtained from the ^{1}H NMR spectrum of a 0.034 mol dm^{-3} solution of $Mg(TMP)_{5.75}(ClO_4)_2$ in a d_6-acetone/acetone mixture in which a broad signal arising from co-ordinated acetone was observed 42 Hz downfield from the free acetone signal at 185 K. In solutions vi) and vii) a single ^{31}P singlet was observed for co-ordinated TMP at 185 K and the integrations were consistent with $Mg(TMP)_6^{2+}$ being the predominant magnesium(II) species in solution.

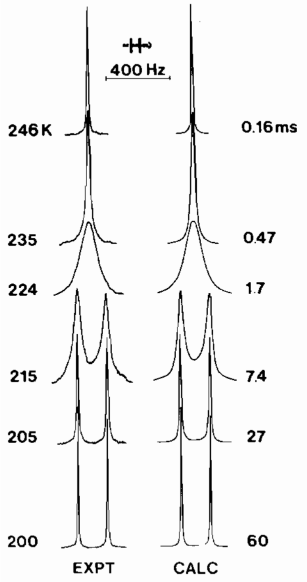

Figure 3. Experimental and computed best fit ^{31}P FT NMR line shapes of a $Mg(TMP)_6^{2+}$ (0.278 mol dm^{-3}), TMP (1.59 mol dm^{-3}) and d_6-acetone (8.06 mol dm^{-3}) solution. The experimental temperatures and best fit τ_B values appear to the left and right of the figure respectively. The free TMP signal is downfield.

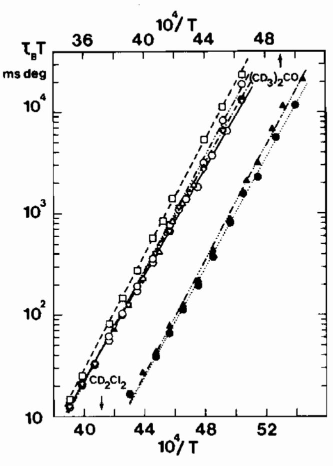

Figure 4. Semilogarithmic plots of $\tau_B T$ against 1/T for the $Mg(TMP)_6^{2+}$ system. The individual data points for solutions i) to vii) are represented as i) ○, ii) △, iii) ▽, iv) ○, v) □, vi) ▲, vii) ● and the corresponding linear least-squares lines (the line for solution iii) is omitted for clarity) as ——, ·—·—·, ··—··—··, — — —, ···—···—···, and ·······. The bottom scale refers to solutions i) to v) while vi) and vii) are referred to the upper scale.

The kinetic parameters characterising the intermolecular exchange of TMP on $Mg(TMP)_6^{2+}$ were determined through a complete line shape analysis [8, 18] of the coalescence of the proton decoupled ^{31}P singlets arising from free and co-ordinated TMP, in d_2-methylenechloride and d_6-acetone diluents, over the temperature range 198–256 K. Best fit two site exchange line shapes and co-ordinated TMP life times (τ_B) were derived through a classical line shape expression using the BNC-12 minicomputer of the Bruker HX90E spectrometer. Typical experimental and best fit line shapes are shown in Figure 3. The kinetic parameters characterising the TMP exchange process are related through equation (1):

$$\tau_B^{-1} = k_{ex} = \text{exchange rate}/6[Mg(TMP)_6^{2+}] =$$

$$kT/h \exp -\Delta H^{\#}/RT \exp \Delta S^{\#}/R \qquad (1)$$

where $\tau_B = \tau_F \chi_B/\chi_F$ and χ_B and χ_F are the mole fractions of bound and free TMP respectively, and all

TABLE 1. Solution Compositions and Derived Parameters for the $Mg(TMP)_6^{2+}$ System.

Solution	$[Mg(TMP)_6^{2+}]$ mol dm^{-3}	$[TMP]_{free}$ mol dm^{-3}	$[CD_2Cl_2]$ mol dm^{-3}	$[(CD_3)_2CO]$ mol dm^{-3}	CN[a]	k_{ex} (225K)[b] s^{-1}	$\Delta H^{\#}$[c] kJ mol^{-1}	$\Delta S^{\#}$[c] J K^{-1} mol^{-1}
i	0.0640	0.327	13.8	–	6.0 ± 0.1	707 ± 42	50.5 ± 0.4	36.2 ± 1.9
ii	0.116	0.604	12.7	–	6.1 ± 0.1	683 ± 47	51.3 ± 0.5	39.5 ± 2.0
iii	0.185	0.970	11.4	–	5.9 ± 0.1	689 ± 47	50.8 ± 0.5	37.2 ± 2.0
iv	0.160	1.61	10.3	–	5.8 ± 0.2	630 ± 41	53.4 ± 0.4	48.1 ± 2.0
v	0.299	2.51	7.07	–	5.9 ± 0.1	442 ± 27	54.1 ± 0.4	48.6 ± 1.9
vi	0.188	0.842	–	10.3	5.8 ± 0.2	495 ± 53	53.8 ± 0.8	48.2 ± 3.4
vii	0.278	1.59	–	8.06	5.9 ± 0.1	587 ± 57	51.2 ± 0.7	38.1 ± 3.3
	[d]$Mg(H_2O)_6^{2+}$	–	–	–	6	1585[g]	42.7	8.4
	[e]$Mg(MeOH)_6^{2+}$	–	–	–	6	0.324[g]	69.9	58.6
	[f]$Mg(EtOH)_6^{2+}$	–	–	–	6	108.4[g]	74.0	125.5

[a] CN = number of co-ordinated TMP molecules as determined from integration of the ^{31}P NMR signals of free and bound TMP in the temperature range 175–195 K. The quoted errors represent one standard deviation. [b] k (225K) interpolated from the Eyring plots. The quoted errors represent one standard deviation. [c] $\Delta H^{\#}$ and $\Delta S^{\#}$ determined from the Eyring plots. The quoted errors represent one standard deviation. [d,e,f] Data from references 11, 9 and 10 respectively. [g] k_{ex} (225 K) values calculated from the literature data.

other symbols have their usual meaning. The composition of each solution and the derived kinetic parameters for each solution studied is given in Table I, and plots of $\tau_B T$ against $1/T$ are shown in Figure 4.

The rate constants derived in the midst of the NMR signal coalescence phenomenon (which occurs at ~225 K in this system) are considered to be the most reliable [18] and hence k_{ex} (225 K) values are quoted here. The k_{ex} (225 K) values for solutions i)–iv) are identical within two standard deviations over a 4.9 fold variation in $[TMP]_{free}$, and the variation in k_{ex} (225 K) over the 7.6 fold variation encompassed by solutions i)–v) is a factor of 1.6. Thus the rate of TMP exchange on Mg(TMP)$_6^{2+}$ is not markedly dependent on $[TMP]_{free}$ in d_2-methylenechloride diluent. Space filling models indicate that approximately 20 methylenechloride molecules or 10 trimethylphosphate molecules can fill the second co-ordination sphere of Mg(TMP)$_6^{2+}$. Hence, on a statistical basis the number of TMP molecules in the second co-ordination sphere of Mg(TMP)$_6^{2+}$ will vary from less than one in solution i) to four or more in solution v). Unless there is a very high degree of preferential occupancy of the second coordination sphere by TMP such that this occupancy is almost invariant under the experimental conditions reported here, it appears that the lability of TMP in the first co-ordination sphere is not modified to a major extent by the composition of the second co-ordination sphere. This is supported by the observation that the kinetic parameters derived from solutions vi) and vii) in d_6-acetone diluent may not be meaningfully distinguished from those observed in d_2-methylenechloride diluent. Overall these rate phenomena are consistent with a TMP exchange mechanism in which bond breaking constitutes the predominant contribution to the observed $\Delta H^{\#}$ and $\Delta S^{\#}$ values. The observation of Mg(TMP)$_5^{2+}$ in d_2-methylenechloride diluent lends support to the postulation of a dissociative ^{2}(D) TMP exchange process for Mg(TMP)$_6^{2+}$ as also do the observations of five co-ordinate MgL$_5^{2+}$ (where L = trimethylarsine oxide or trimethylphosphine oxide) in the solid state [15, 16].

As a consequence of the large ^{31}P chemical shift between free and co-ordinated TMP (5.70 ppm compared to 0.07 ppm in the earlier ^{1}H study) and the consequently greater temperature range (198–256 K compared to 188–198 K in methylenechloride and 193–208 K in acetone in the ^{1}H study) the kinetic parameters reported here are considered to be more reliable than the earlier ^{1}H data reported for this system. These new $\Delta H^{\#}$ and $\Delta S^{\#}$ data lie close to the $\Delta H^{\#}/\Delta S^{\#}$ linear free energy line recently published [7] for solvent exchange on divalent metal ions of similar ionic radii for which D or I_D mechanisms are thought to operate, and which also probably indicates [3, 5, 7] that surface charge density of the metal ion is a major factor determining the magnitude of $\Delta H^{\#}$ and $\Delta S^{\#}$. It is seen from Table I that the kinetic parameters for the Mg(TMP)$_6^{2+}$ system fall in the midst of the range encompassed by the analogous water [11], methanol [9] and ethanol [10] systems for which D exchange mechanisms have also been suggested.

Acknowledgements

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References

1 K. Kustin and J. Swinehart, *Prog. Inorg. Chem., 13,* 107 (1970).
2 C. H. Langford and H. B. Gray, "Ligand Substitution Processes", W. A. Benjamin, New York (1966).
3 J. P. Hunt, *Coord. Chem. Rev., 7,* 1 (1971).
4 S. Funahashi and R. B. Jordan, *Inorg. Chem., 16,* 1301 (1977).
5 H. P. Bennetto and E. F. Caldin, *J. Chem. Soc. A,* 2198 (1971).
6 D. R. Stranks, *Pure Appl. Chem., 38,* 303 (1974).
7 J. Crea, R. Diguisto, S. F. Lincoln, and E. H. Williams, *Inorg. Chem., 16,* 2825 (1977).
8 J. Crea, S. F. Lincoln and R. J. West, *Austral. J. Chem., 26,* 1227 (1973).
9 S. Nakamura and S. Meiboom, *J. Am. Chem. Soc., 89,* 1765 (1967).
10 T. D. Alger, *J. Am. Chem. Soc., 91,* 2220 (1969).
11 J. Neely and R. Connick, *J. Am. Chem. Soc., 92,* 3476 (1970).
12 N. M. Karayannis, C. Owens, L. L. Pytlewski, and M. M. Labes, *J. Inorg. Nucl. Chem., 81,* 2059 (1969).
13 P. W. N. M. van Leeuwen and W. L. Groeneveld, *Inorg. Nucl. Chem. Lett., 3,* 145 (1967).
14 A. I. Vogel, "Quantitative Inorganic Analysis", 3rd ed., Longmans Green and Co., London (1961) p. 702.
15 Y. S. Ng, G. A. Rodley, and W. T. Robinson, *Inorg. Chem., 15,* 303 (1976).
16 Y. S. Ng, W. T. Robinson, and G. A. Rodley, reported at the 7th Coordination and Metal Organic Chemistry Division Conference of the Royal Australian Chemical Institute, La Trobe University, Victoria, Australia, February (1977).
17 F. Toma, M. Villemin, and J. M. Thiéry, *J. Phys. Chem., 77,* 1294 (1973).
18 S. F. Lincoln, *Prog. Reaction Kinetics, 9,* 1 (1977).